

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Ammonia

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Wilmington 98, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is for improvements in or relating to the catalytic synthesis of ammonia from gaseous nitrogen and hydrogen.

The Haber process for the preparation of ammonia from gaseous hydrogen and nitrogen is an extremely important industrial reaction. By this process, gaseous nitrogen and hydrogen in a molar ratio of 1 to 3 are brought together in the presence of a suitable catalyst to form ammonia as represented by the following equation.



The reaction is reversible and, as shown by the above equation, is highly exothermic. Therefore, in accordance with Van't Hoff's Law, an increase in temperature favours the reverse reaction, i.e. the dissociation of ammonia into nitrogen and hydrogen. It is thus apparent that the higher the temperature employed, the smaller the amount of ammonia in the equilibrium mixture. For this reason it is desirable to run the reaction at low temperatures. The difficulty with this is that the speed of the reaction is directly proportional to the temperature, i.e., the lower the temperature, the slower the reaction even in the presence of a catalyst. At room temperature there is no noticeable reaction between the gases. At the present time, it is not practical to perform this synthesis at temperatures lower than about 450° C.

Since the reaction is accompanied by a volume decrease (4 moles of gas react to produce 2 moles of gaseous ammonia), high pressures tend to favour the production of

ammonia rather than the reverse reaction. However, there are practicable limitations on the pressures which may be used. As the pressure increases, the permeability of the reactor to hydrogen increases and the tendency of the hydrogen to embrittle the metal increases also.

Much research has been conducted in recent year to discover catalysts which would make possible the use of lower temperatures in this synthesis, without unduly decreasing the reaction rate. Up to the present time, this research has not been very fruitful. The best catalyst now available from the standpoint of efficiency, ruggedness, and cost is an iron-iron (II and III) oxide-potassium aluminate. With this catalyst, temperatures of about 450—600° C. and pressures of from 300 to 1000 atmospheres are generally required to provide a practical rate of reaction.

It is an object of the present invention to provide an improved process for the synthesis of ammonia from gaseous nitrogen and hydrogen. It is an additional object of the invention to provide a novel catalyst for use in such a synthesis. It is a still further object of the invention to provide a catalytic process for the synthesis of ammonia from gaseous nitrogen and hydrogen which can be run efficiently at lower temperatures than has heretofore been feasible.

According to one aspect of the present invention, a process for the synthesis of ammonia from gaseous nitrogen and hydrogen comprises contacting the gases in the presence of a catalyst comprising a transition metal oxide which has been heated in an inert atmosphere to a temperature of 450° to 600° C. in the presence of an alkali metal. Employing such process, it has proved possible to synthesize ammonia from gaseous nitrogen and hydrogen at temperatures well below 450° C. and pressures much lower than 600 atmospheres while maintaining the contact time at less than 100 seconds and frequently less than 50 seconds.

As stated above, the catalyst employed is

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to 60

a transition metal oxide-alkali metal composition. The catalyst may be unextended or it may be extended on alumina. The unsupported catalyst may be conveniently prepared by simply mixing the transition metal oxide and the alkali metal and heating at temperatures from 450° to 600° C. in an inert atmosphere.

An exemplary technique for preparing the extended catalyst, using a salt of the transition metal which is directly convertible to the oxide, is as follows:

The alumina support is impregnated with a solution of an organic or an inorganic salt of the transition metal, and the impregnated support is then heated in air to convert the transition metal salt to the oxide. The resulting product is then placed in a nickel tube about 24 inches long and 1 inch in diameter which is welded shut at one end. The alkali metal is placed at the bottom of the tube in a one-half inch diameter nickel pipe which is three inches long. A 100-mesh stainless steel screen is then affixed to the upper end of the small tube. A thermocouple well is placed within the larger tube so that it extends to the surface of the screen. The transition metal-impregnated support is placed within the larger tube and the assembly is connected to a vacuum train. The system is evacuated at about 0.3 mm. and the portion containing the transition metal-impregnated support is heated to 500° C. \pm 15° C. The portion of the tube containing the alkali metal is heated under vacuum, to distill the alkali metal through the extended transition metal oxide, for from about 1 to 20 hours. Thereafter the composition is permitted to cool in an inert atmosphere, e.g., helium or argon. It is then removed from the reactor under a blanket of the inert atmosphere and stored under a blanket of the inert atmosphere.

As used herein, the term "alkali metal" is intended to include the elements lithium, sodium, potassium, rubidium, and cesium. Of these, sodium is preferred because of its ready availability and relatively low cost. The amount of alkali metal should be at least about 1% by weight, based on the transition metal oxide present in the catalyst composition. Generally speaking, more active catalysts are obtained when the alkali metal content of the composition is in the range of about 5—300% by weight of the transition metal oxide present.

As used herein, the term "transition metal" is intended to include scandium, yttrium and lanthanum from Group III-A of the Periodic Table of Elements; titanium, zirconium, and hafnium from Group IV-A; vanadium, niobium and tantalum from Group V-A; chromium, molybdenum and tungsten from Group VI-A; manganese from Group VII-A and all of the Group VIII metals. Preferably, said metal is molybdenum, vanadium, chromium,

cobalt or iron.

The alumina support may be a commercial preparation or it may be an alumina prepared by dehydrating hydrous alumina, as described in Ind. Eng. Chem. 42, 1938 (1950), in United States Patent 2,453,327, or by H. D. Weiser in his "Colloid Chemistry," John Wiley and Sons, Inc., New York (1949, 2nd Ed) or by gel precipitation from salt solutions as disclosed in United States Patent 2,432,286, or from metallic aluminium as disclosed in Specification No. 552,053.

The ammonia concentration in the product stream depends upon a variety of reaction conditions including temperature, pressure, nature of catalyst, and feed rates of nitrogen and hydrogen. The reaction conditions are carefully adjusted to yield the highest possible ammonia concentration in the reaction which is consistent with a practical reaction rate.

Although ammonia is produced at temperatures as low as about 200° to 220° C. (see for instance Examples III and IV), practical reaction rates are not attained until the temperature is at least about 300° C. For reasons of economy, it is therefore preferred to carry out the reaction at temperatures which are in the range of about 300° to 450° C. and preferably within 300° to 400° C.

As noted above, the formation of ammonia is favoured by an increase in pressure since the reaction is accompanied by a volume decrease. In practice, the process of the invention is usually operated under superatmospheric pressures up to about 600 atmospheres. Higher pressures are not used because of difficulties with permeability and embrittlement of the metal reactor. The preferred pressure is within the range of 100—300 atmospheres.

The contact time of the reaction gases with the catalyst will vary considerably depending upon the specific temperature and pressure employed, the catalyst volume, and on the feed rate of the gases. In practice these variables are adjusted so that the contact time is within the range of about 0.02 to 100 seconds and preferably within 0.5 to 50 seconds. The temperatures and pressures specified in the preceding paragraphs are consistent with a contact time within this range.

With the reaction conditions outlined above the space velocity of the reaction gases is generally above about 500 reciprocal hours. For practical reasons, space velocities in excess of about 25,000 reciprocal hours are rarely used.

The amount of catalyst used in any particular instance is dependent upon all the other variables such as temperature, pressure, activity of the catalyst, contact time, and space velocity. As a rule, the amount of catalyst used is that which makes possible the contact time and space velocity indicated

above at the moderate temperatures and pressures which are employed.

5 The hydrogen gas used in the process of the invention may be preformed as illustrated in the Examples which follow, or it may be formed *in situ*, e.g. by pyrolysis of hydrocarbons. Neither of these arrangements is in any sense critical to the invention.

10 It is contemplated that the process of the invention may be operated as a continuous vapour phase operation with recycling (and refortifying) of the unreacted gases. The ammonia which is formed can be removed by absorption in water or dilute acid, or it can be liquefied by refrigeration or by a compression-expansion system. The liquefaction method will be preferred in many instances since the ammonia is obtained as such rather than in aqueous solution or as a salt.

20 The process of the present invention is a distinct improvement over the prior catalytic syntheses of ammonia from gaseous nitrogen and hydrogen. It makes possible the attainment of the desired product at favourable reaction rates under conditions which are significantly less severe than those of prior art processes. The short reaction times and relatively mild temperatures and pressures which are feasible with the process are extremely important from a commercial standpoint. The lower the temperature and the pressure, the less power is required and the useful life of the production equipment is extended accordingly. The cost of synthesising ammonia with a catalytic process of this type is directly dependent upon such factors.

30 The invention includes within its scope, as a new catalyst especially suitable for the catalytic conversion to ammonia of a gaseous mixture of hydrogen and nitrogen, a transition metal oxide which has been heated in an inert atmosphere to a temperature of at least about 500° C. in the presence of an alkali metal.

45 The invention is illustrated by the following Examples:

EXAMPLE I

50 100 Grams of gamma-alumina ($\frac{1}{8}$ inch mesh) was added to 20 grams of ammonium molybdate in 500 ml. of water at 35° C. The solid product, molybdenum trioxide-on-alumina, was isolated by filtration, washed with water, and dried at 475–500° C. for 12 hours. The product was found to contain 5.03% molybdenum. 5 Grams of sodium and 50 grams of the molybdenum trioxide-on-alumina were charged into the apparatus described above. After sliding a two-hole rubber stopper into place around the thermocouple, the assembly was evacuated through the second hole of the stopper to 0.3 mm. The section of the assembly containing the catalyst was heated to 450–500° C. to degas and remove residual water. The pressure rose

to 1.5 to 2 mm. and gradually fell back to 0.3 mm. within an hour. After degassing was complete, the lower section of the tube was heated to 450° C. to effect distillation of the sodium through the overlying supported oxide. After five hours the reactor was cooled and brought to atmospheric pressure with argon. The product was sealed in glass ampoules under argon. It was found to contain 4.64% Na and 4.66% Mo, and was amorphous by X-ray analysis.

70 This technique for extending the catalyst is not critical to the invention, and there are several other methods that may be used which are just as satisfactory. Similarly, the shape or configuration of the extended catalyst is not critical. The extended catalyst may be used in the form of spherical or cylindrical pellets or any other suitable shape.

85 In commercial practice, the catalyst described above would be used in a furnace equipped with heating means and capable of withstanding pressures up to 1000 atmospheres, or more. A hydrogen/nitrogen mixed gas containing 3 moles of hydrogen per mole of nitrogen would be fed at a space velocity of desirably at least about 500 reciprocal hours over the catalyst which is maintained at a temperature of about 200° to 450° C. and under a pressure which may vary up to 600 atmospheres. The exit gas would be cooled to room temperature and the ammonia separated from unconverted hydrogen and nitrogen by absorption in water, by cooling in a carbon dioxide/acetone trap, or other means known to those skilled in the art. Unreacted hydrogen and nitrogen gas could be enriched and recycled. In the laboratory, the process may be conducted with simpler equipment.

100 The following Examples illustrate the novel ammonia synthesis:

EXAMPLE II

110 A 6.6 g. sample of catalyst composed of sodium-treated molybdenum trioxide supported-on-alumina, prepared as described in Example I, was placed in a heated section of a glass apparatus of such design that it could be filled with gas, which could then be circulated over the catalyst in a closed loop. The system was evacuated and filled with a mixture of hydrogen and nitrogen gas in 3:1 mole ratio to a pressure of slightly over one atmosphere. The catalyst was then heated while the gas was being circulated. After 15 minutes at 300° C. a sample of gas was found to be alkaline to a pH indicator paper, which showed that ammonia was being formed. When the catalyst had been heated to 400° C. for 45 minutes, the gas was even more strongly alkaline, and ammonia could be smelled in a sample of the gas.

125 Following the procedure described in Example II, a series of similar experiments were run with a variety of alumina-supported alkali metal transition metal oxide catalysts: 130

Ex.	Reducing Metal	Transition Metal Oxide	% Reducing Metal in Catalyst	% Transition Metal in Catalyst	Lowest Temperature at which ammonia formation was detectable
III	Na	MoO ₃	4.64	4.66	220°
IV	Na	V ₂ O ₅	7.3	2.86	220°
V	Na	CrO ₃	6.50	1.24	350°
VI	Na	CoO	7.7	2.57	350°
VII	K	MoO ₃	16.3	4.46	250°
VIII	Li	MoO ₃	3.8	4.89	400°

The catalysts in Examples III to VIII were all prepared in accordance with the procedure described in Example I. In Examples III, VII, and VIII, the alumina was impregnated with 20 grams of ammonia molybdate in aqueous solution; in Example IV, with 23.5 grams of ethyl vanadate in aqueous solution; in Example V, with 43 grams of ammonium chromate in aqueous solution; and in Example VI, with 20 grams of cobalt nitrate. In each case, the pyrolysis was effected at 450°—500° C. The catalyst in each Example contained the indicated reducing metals and transition metals in the amounts specified.

EXAMPLE IX

A 7 gram sample of a catalyst similar to that of Example I was placed in a glass tube in a furnace so arranged that 3:1 hydrogen/nitrogen mixed gas could be continuously passed at atmospheric pressure over the catalyst and then exhausted for analysis. The concentration of ammonia in the product stream was determined by measuring the length of time required for the gas, flowing at a known rate, to neutralize a given quantity of dilute hydrochloric acid containing methyl red indicator. At a space velocity of approximately 2000 reciprocal hours, ammonia was formed as follows:

Temp. °C.	% NH ₃ Actually Formed	% NH ₃ at Theoretical Equilibrium	% of Theoretical
350	0.1	0.90	11
400	0.1	0.44	23
450	0.2	about 0.2	100

In the absence of the catalyst of the present invention no ammonia is formed within the temperature range of 350°—450° C.

EXAMPLE X

A 23 gram sample of the catalyst of Example I was placed in a 400 ml. steel pressure vessel. After evacuation, the reactor was pressured with 3:1 hydrogen/nitrogen mixed gas to 600 atmospheres, and heated to 350° C. After agitation for several hour the reactor was allowed to cool, and the contents were bled off through gas washing bottles filled with a measured quantity of standard acid. Based on the ammonium chloride formed, product gas contained 6% ammonia, or 8% of the amount that would be expected if full

equilibrium were reached at 350° C. and 600 atmospheres pressure.

The activating effect of the alkali metal on an unsupported metal catalyst was demonstrated as follows:

EXAMPLE XI

Ferrous hydroxide gel was prepared by precipitation of 70 g. of FeSO₄·7H₂O in 700 ml. of water with 21.5 g. of NaOH in 300 ml. of water. The precipitate was washed by decantation, dried at 70° C. in a vacuum oven, and put through a 20-mesh screen. A portion corresponding to about half of this product was hydrogenated by treatment with hydrogen gas at one atmosphere pressure and 400—480° C. for five hours. The product

was a pyrophoric black powder which did not catalyse formation of ammonia from a $3\text{H}_2:1\text{N}_2$ mixed gas at temperatures up to 400°C . by the procedure of Example II.

- 5 About 200 mg. of sodium metal in small pieces was mixed with the hydrogenated product, and the mixture heated to 600°C . in a nitrogen atmosphere for one hour. The resulting product was then found to catalyse the formation of ammonia from a mixture of hydrogen and nitrogen at 300°C .

WHAT WE CLAIM IS:—

1. A process for the synthesis of ammonia from gaseous hydrogen and nitrogen which comprises contacting the gases in the presence of a catalyst comprising a transition metal oxide which has been heated in an inert atmosphere to a temperature of 450° to 600°C . in the presence of an alkali metal.

2. A process as claimed in claim 1 wherein the reaction in the presence of a transition metal oxide-alkali metal catalyst is effected for not less than 0.02 nor more than 100 seconds at a temperature between 200°C . and 450°C . and a pressure not exceeding about 600 atmospheres.

3. A process as claimed in claim 1 or 2 wherein the reaction temperature is in the range of 300° — 450°C . and the pressure is in the range of about 100—600 atmospheres.

4. A process as claimed in any one of the preceding claims wherein the reaction time is from 0.5 to 50 seconds, the reaction temperature between about 300° — 400°C . and the reaction pressure 100 to 300 atmospheres.

5. A process as claimed in any one of the preceding claims wherein the transition metal oxide is an oxide of molybdenum, vanadium, chromium, cobalt or iron.

6. A process as claimed in any one of the preceding claims wherein the alkali metal is sodium.

7. A process as claimed in any one of the preceding claims wherein the alkali metal is present in amount at least equal to 1% by weight based on the transition metal oxide content.

8. A process as claimed in claim 7 wherein the amount of alkali metal content is in the range of 5 to 300% by weight based on the transition metal oxide content.

9. A process as claimed in any one of the preceding claims wherein the catalyst is formed by heating the transition metal oxide to a temperature of 450° — 600°C . in the presence of the alkali metal and during formation and prior to use is maintained in an inert atmosphere.

10. A process as claimed in claim 9 wherein the catalyst is employed in extended form on an alumina support.

11. For use in the process claimed in any one of the preceding claims, a catalyst comprising a transition metal oxide which has been heated in an inert atmosphere to a temperature of 450° to 600°C . in the presence of an alkali metal.

12. A catalyst as claimed in claim 11 wherein the transition metal oxide is an oxide of molybdenum, vanadium, chromium, cobalt or iron.

13. A catalyst as claimed in claim 11 or 12 wherein the alkali metal is sodium.

14. A catalyst as claimed in claim 11, 12 or 13 wherein the transition metal oxide is extended on an alumina support.

15. A process as claimed in claim 1 when carried out substantially as described in any one of the foregoing Examples.

16. A catalyst as claimed in claim 11 substantially as described in any one of Examples I, III to VIII and XI.

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